

## STABLE CHLORINE ISOTOPE STUDY; APPLICATION TO EARLY SOLAR SYSTEM MATERIALS.

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**Introduction:** A significantly large mass fractionation between two stable chlorine isotopes is expected during planetary processes. In addition, in view of the isotopic heterogeneity of other light elements, the chlorine isotopes can potentially be used as a tracer for the origins and evolutionary processes of early solar system materials. Due to analytical difficulties, however, current chlorine isotope studies on planetary materials are quite controversial among IRMS (gas source mass spectrometry) and/or TIMS (Thermal Ionization Mass Spectrometry) groups [i.e. 1-3]. Although a cross-calibration of IRMS and TIMS indicates that both techniques are sufficiently consistent with each other [4], some authors have claimed that the  $^{37}\text{Cl}/^{35}\text{Cl}$  ratio of geological samples obtained by TIMS technique are, in general, misleadingly too high and variable compared to those of IRMS [3]. For example, almost no differences of Cl isotope composition were observed among mantle materials and carbonaceous meteorites by [3]. On the other hand, according to more recent IRMS work [2], significant Cl isotope variations are confirmed for mantle materials. Therefore, additional careful investigation of Cl isotope analyses are now required to confirm real chlorine isotope variations for planetary materials including carbonaceous chondrites [5].

In order to clarify the stable chlorine isotope features of early solar system materials, we have initiated development of the TIMS technique at NASA JSC applicable to analysis of small amounts of meteoritic and planetary materials. We report here the current status of chlorine isotope analysis at NASA JSC.

**Analytical Technique:** For silicate samples, a HF-leaching method modified from that of Musashi et al [6] was employed in this work. The sample was subjected to 24 hrs shaking in HF solution, then to neutralization and  $\text{CaF}_2$  precipitation by  $\text{Ca}(\text{OH})_2$  slurry, and again to shaking for several hours to reach equilibrium [6]. The recovery yield of this process (obtained by ion chromatography measurement) was found to be almost 100%. Chlorine was recovered as AgCl from the sample solution, converted to ammoniacal complex and to  $\text{MgCl}$  by reaction with metallic Mg, and finally to cation-resin (AG 50Wx8 200-400 mesh) treatment to yield CsCl [7]. The total chemical yield of chlorine was about 90%. We noted that 10% or more losses of chlorine was caused mainly by the difficulty of handling of

small amounts of AgCl precipitates (50-100  $\mu\text{gCl}$ ; 200-400  $\mu\text{g}$  as AgCl) in a dark room.

The CsCl (2  $\mu\text{g Cl}$ ) was loaded on a wide Ta filament together with an emitter (fine-grained graphite) in a way similar to our previous work [7]. In order to establish well-qualified TIMS techniques, we have investigated more detailed conditions of mass spectrometry using  $^{133}\text{Cs}_2^{35,37}\text{Cl}^+$  ions ( $^{133}\text{Cs}^+$  and  $^{133}\text{Cs}_2^{19}\text{F}^+$  ions are also monitored). We have performed repeated runs of a laboratory isotope standard (Nacalai tesque CsCl reagent), seawater, standard rocks (JB-2 and JB-3) and a few meteorite samples in different experimental conditions.

**Definition of Cl isotope composition:** The isotopic variations of chlorine are defined as permil deviation from seawater (SMOC: Standard Mean Ocean Chloride).  $\delta^{37}\text{Cl}(\text{‰})_{\text{SMOC}} \equiv \{[^{37}\text{Cl}/^{35}\text{Cl}]_{\text{Sample}} / [^{37}\text{Cl}/^{35}\text{Cl}]_{\text{Seawater}} - 1\} \times 10^3$

**Results and Discussion:** The isotopic composition of our laboratory standard was well established in our previous work;  $\delta^{37}\text{Cl}_{\text{SMOC}} = -2.49 \pm 0.21\text{‰}$  [7]. In order to detect any change of mass spectrometric condition, we normally analyse Cl standard before, between and after the unknown samples. Since we have employed the HF-leaching method similar to that of Musashi et al. [6], it is interesting to compare our

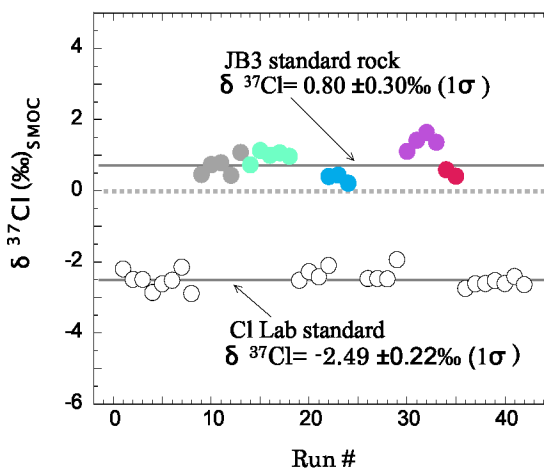


Fig. 1 Preliminary results for JB3 standard rock and Cl laboratory standard (Nacalai tesque CsCl reagent). Individual data points represents the mean of 300 ratios/run.

TIMS results for the same standard rock, JB3, with Musashi's analysed by their IRMS technique. We have carried out 20 runs of JB3 (5 separate loadings) together with 23 runs (4 separate loadings) of Cl standard. As shown in Fig. 1, the mean of  $\delta^{37}\text{Cl}$  (‰)<sub>SMOC</sub> =  $0.80 \pm 0.30$  ( $1\sigma$ ) was obtained in this work. This value is in agreement with Musashi's ( $0.55 \pm 0.10$ ) within  $1\sigma$  error. Although our JB3 analyses are still limited and so contain relatively large errors, it is worth noting that both TIMS and IRMS results are in good agreement. In addition to our preliminary work on bulk chondrites [5], analyses of Allende and other carbonaceous chondrites are now in progress.

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**References:** [1] Bonifacie M. et al. (2007) *Chem Geol*, 242, 187-201. [2] Bonifacie M. et al. (2008), *Science* 319, 1518-1520. [3] Sharp Z. D. et al. (2007), *Nature* 446, 1062-1614. . [4] Godon A. et al (2004) *Chem. Geol.* 207, 1-12. [5] Nakamura N. et al. (2007) *LPS XXXIII* #1929 [6] Musashi M. et al. (1998), *Anal. Chim. Acta* 362 261-269. [7] Numata M. et al. (2001), *Geochem. J.* 35, 89-100.